

## **2.2. MASS SPECTROMETRY**

### **Structure :**

- 2.2.1. Introduction
- 2.2.2. Instrumentation
- 2.2.3. ION Production
- 2.2.4. Types of Ionization
- 2.2.5. Fragmentation of Organic Compounds
- 2.2.6. Meta Stable Peak
- 2.2.7. Mc Lafferty Rearrangement
- 2.2.8. The Nitrogen Rule
- 2.2.9. Halogen Compounds
- 2.2.10. Alkanes
- 2.2.11. Alkenes
- 2.2.12. Alkyl Aromatic Compounds
- 2.2.13. Ethers
- 2.2.14. Alcohols
- 2.2.15. Ketones
- 2.2.16. Suggested Readings

## 2.2. MASS SPECTROMETRY

### 2.2.1. Introduction :

Mass spectrometry is one of the most versatile technique used to characterize organic compounds. It is also useful method for determining the molecular mass of the compound and its elemental composition. In this technique, the molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge (i.e.)  $m/e$  ratio. In mass spectrum a signal is obtained for each value of  $m/e$  that is represented. The intensity of each signal represents the relative abundance of the ion producing the signal. The largest peak in the spectrum is called the base peak and its intensity is taken as 100. The intensities of other peaks are represented relative to the base peak.

Mass spectra is used in the following two general ways :

- i) To prove the identity of two compounds
- ii) To establish the structure of a new compound

**2.2.2. Instrumentation :** Mass spectrometers of both low and high resolution are available. A typical  $180^\circ$  single focusing low resolution mass spectrometer shows the following components.

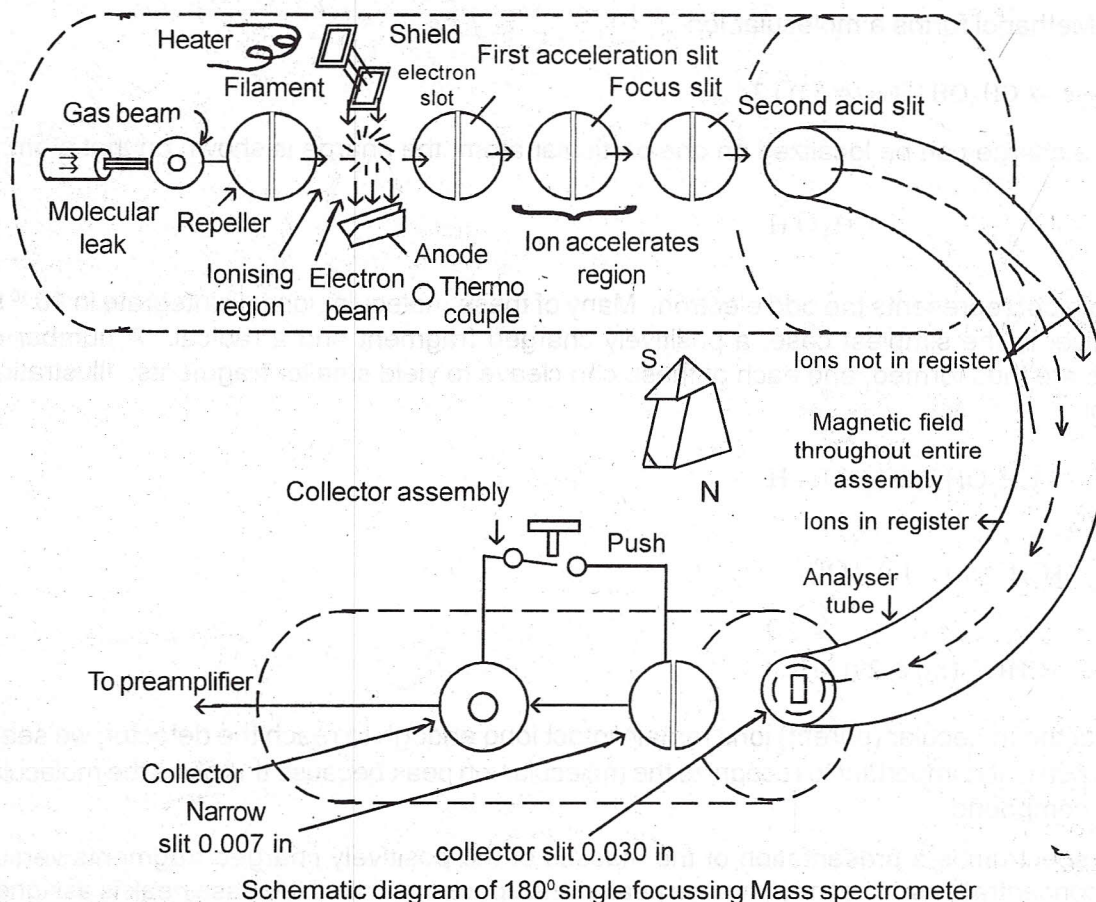
**1. Sample Handling System :** This consists of a device for introducing the sample, a micromanometer for determining the amount of sample introduced, a device (molecular leak) for metering the sample to the ionization chamber and a pumping system. Sample sizes for liquids and solids range from several milligrams to less than a microgram, depending on the method of introduction and the detector. For routine work, vapour pressure of  $10^{-1}$  to  $10^{-3}$  torr is desired.

**2. Ionization and Accelerating chambers :** The gas stream from the molecular leak enters the ionization chamber in which it is bombarded at right angles by an electron beam emitted from a hot filament. Positive ions produced by interaction with the electron beam are forced through the first acceleration slit by a small electrostatic field between the repellers and the first acceleration slit. A strong electrostatic force between the first and second accelerating slits accelerates the ions to their final velocities. To obtain a spectrum, either the magnetic field applied to the analyzer tube or the accelerating voltage between the first and second ion slits is varied. Thus the ions are focussed at the collector slit as a function of mass.

**3. Analyzer Tube and Magnet :** The analyzer tube is an evacuated, curved, metal tube through which the ion beam passes from ion source to the collector. The magnetic pole pieces are mounted perpendicular to the plane of the diagram. The main requirement is a uniform and stable magnetic field.

**4. Ion Collector and Amplifier :** A typical ion collector consists of one or more collimating slits and a faraday cylinder; the ion beam impinges axially into the collector, and the signal is amplified by an electron multiplier.

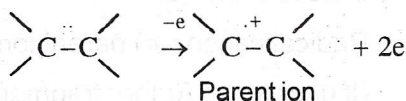
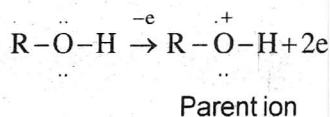
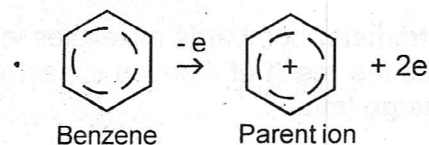
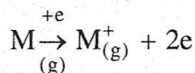
**5. Recorder :** A widely used recorder uses five separate galvanometers that record simultaneously. Peak heights are proportional to the number of ions of each mass.



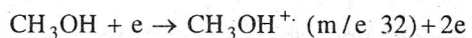
Schematic diagram of 180° single focussing Mass spectrometer

### 2.2.3. ION Production :

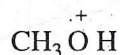
Mass spectra are routinely obtained at an electron beam energy of 70 e.v. The simplest event that occurs is the removal of a single electron from the molecule in the gas phase by an electron of the electron beam to form a molecular ion, which is a radical cation ( $M^+$ ). The highest occupied orbital of aromatic system and non bonding electron orbitals on Oxygen and Nitrogen atoms readily lose one electron. An electron from double bond or triple bond is usually lost. In alkanes the ionization of C-C sigma bond is easier than that of C-H bonds.



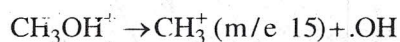
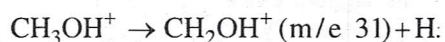
For ex : Methanol forms a molecular ion



When the charge can be localized on one particular atom, the charge is shown on that atom.



The single dot represents the odd electron. Many of these molecular ions disintegrate in  $10^{-10}$  to  $10^{-3}$  Sec to give, in the simplest case, a positively charged fragment and a radical. A number of fragment ions are thus formed, and each of these can cleave to yield smaller fragments. Illustrating with methanol.



If some of the molecular (parent) ions remain intact long enough to reach the detector, we see a molecular ion peak. It is important to recognize the molecular ion peak because this gives the molecular weight of the compound.

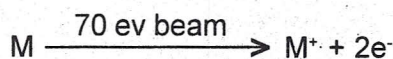
A mass spectrum is a presentation of the masses of the positively charged fragments versus their relative concentrations. The most intense peak in the spectrum, called the base peak is assigned a value of 100% and the intensities of the other peaks, including the molecular ion peak, are reported as percentages of the base peak. Sometimes the molecular peak may be the base peak.

#### 2.2.4. Types of Ionization :

There are four types of Ionization methods.

1. Electron Impact mode
2. Chemical ionization method
3. Field desorption
4. Fast atom bombardment

**1. Electron Impact Mode :** In this method a mass spectrometer bombards molecules in the vapour phase with a high – energy electron beam and records the result of electron impact as a spectrum of positive ions separated on the bases of mass | charge (m/z)



Molecular ion (or)

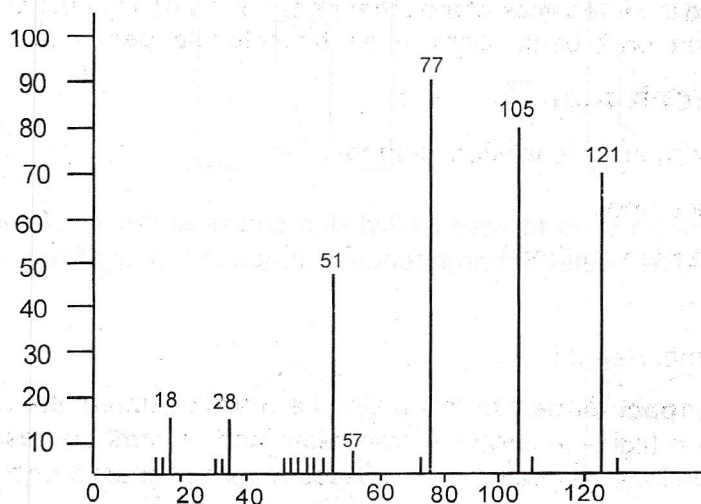
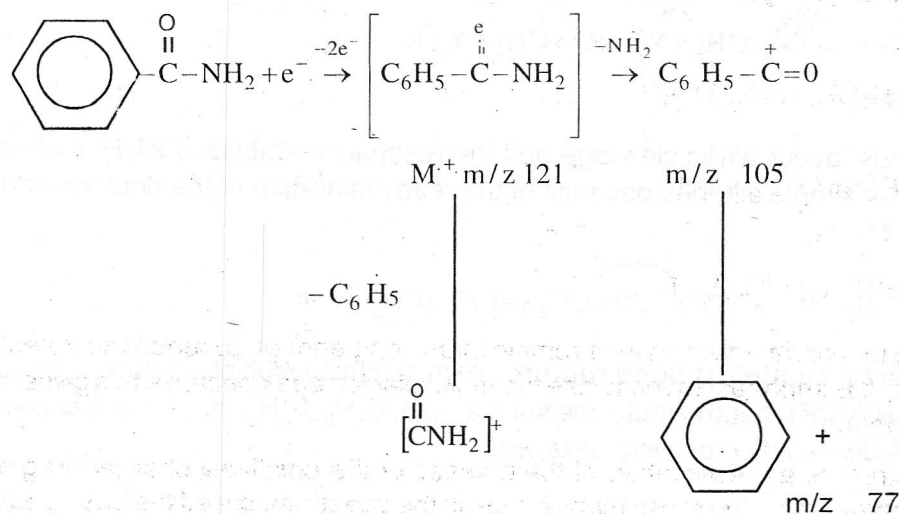
Radical cation (or) parent ion.

(It undergoes further fragmentation)

Sufficiently stable molecular ion cannot be formed by this method. This is because of large amount of excess energy imparted to the molecular ion by 70eV bombardment.

**Base peak** : A mass spectrum is a presentation of the masses of the positively charged fragments versus their relative concentrations. The largest peak in the spectrum, called the base peak. Its intensity is taken as 100% and the intensities of other peaks, including the molecular ion peak, are reported as percentages of the base peak. The molecular ion peak may sometimes be the base peak. In the below example molecular ion peak is  $m/z$  '121', and base peak is  $m/z$  77.

Eg :

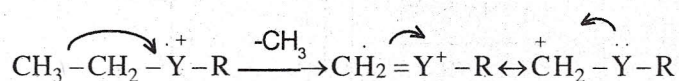


### 2.2.5. Fragmentation of Organic Compounds :

**I Bond rupture in alkane group** : This can really only be represented by assuming that, at the instant of ionization, sufficient excitation energy is concentrated on the rupturing bond to ionize it.

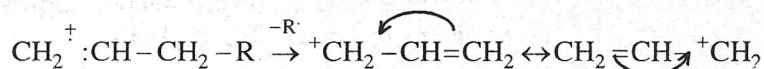
Cleavage is favoured at alkyl substituted carbon atoms, the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbocation over a secondary, which in turn is more stable than a primary. Generally, the largest substituent at a branch is eliminated most readily as a radical, because a long - chain radical can achieve some stability by delocalization of the lone electron.

**II  $\sigma$  Bond rupture near functional groups :** This is facilitated by the easier ionization of non bonding orbitals of hetero atom than the  $\sigma$  bonding orbitals. The C-C bond next to a hetero atom are frequently cleaved, leaving the charge on the fragment containing the hetero atom whose non bonding electrons provide resonance stabilization.

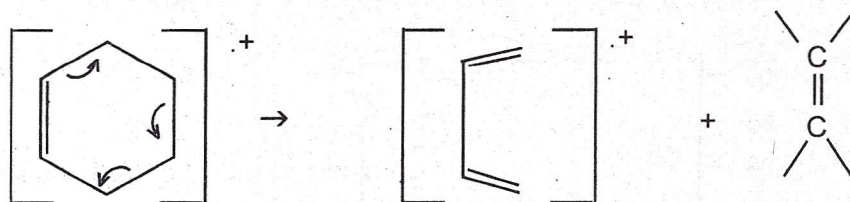


Y=O, NH, or S.

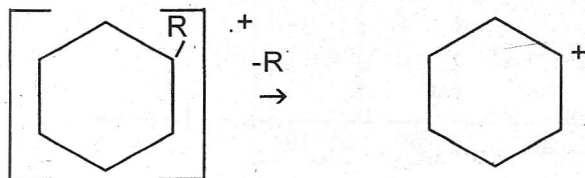
**III** Double bonds favour allylic cleavage and the resonance stabilized allylic carbocation. This rule does not hold for simple alkenes because of the ready migration of the double bond, but it does hold for cycloalkenes.



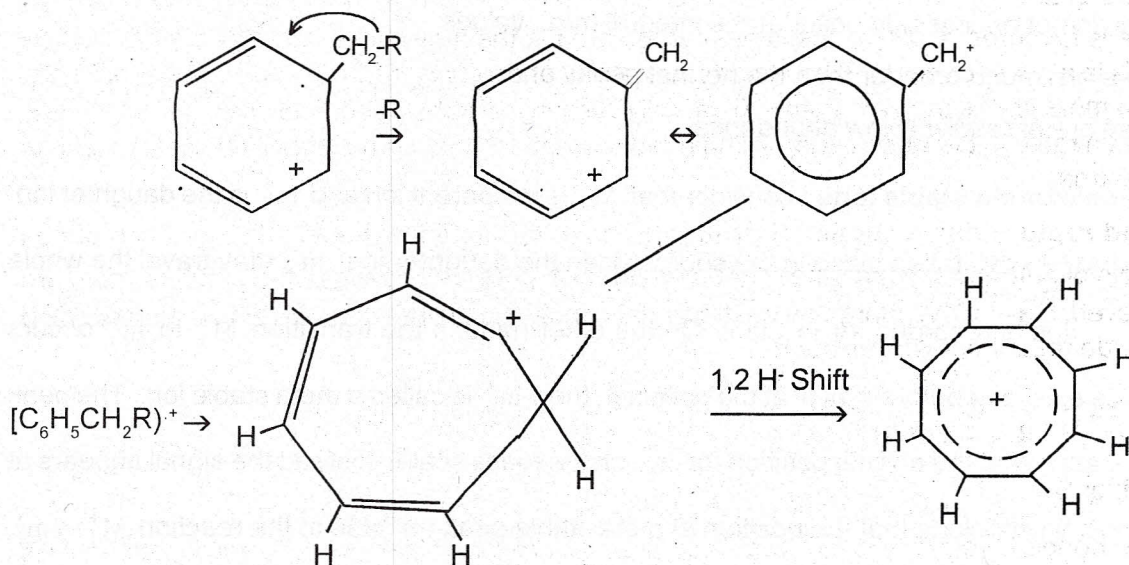
**IV Elimination by multiple  $\sigma$  bond rupture :** Elimination by multiple  $\sigma$ -bond rupture may occur, leading to the extrusion of a neutral molecule such as CO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, etc,. A well known example is the Retro -Diels - Alder reaction of cyclohexenes.



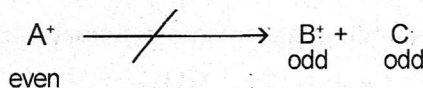
**V) Saturated rings tend to lose :** Alkyl side chains at the ' $\alpha$ ' bond. This is merely a special case of branching. The positive charge tends to stay with the ring fragment.



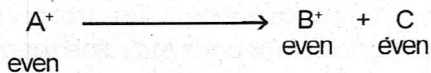
VI) In alkyl - substituted aromatic compounds, cleavage is very probable at the bond  $\beta$  to the ring giving the resonance - stabilized benzyl ion or, more likely, the tropylium ion.



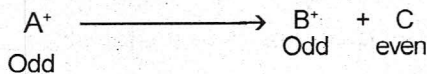
**VI) Even Electron Rule :** This is based on thermodynamic principles. It states that an even electron species will not normally fragment to two odd electron species i.e., an ion will not fragment to a radical and a radical ion since the total energy of this product mixture will be too high.



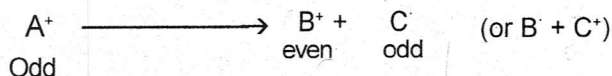
In Preference, an ion will degrade to another ion and a neutral molecule.



Radical ions, being odd – electron species, can extrude a neutral molecule, leaving a radical ion as co product.



Radical ions can also degrade to a radical and an ion



VII) Some times cleavage is often associated with rearrangement.

Eg. Mc Lafferty rearrangement in carbonyl compounds

**2.2.6. Meta Stable Peak :** Meta stable peaks can be easily determined in a mass spectrum. Some important characteristics of these peaks are :

- i) They do not necessarily occur at the integral  $m/e$  values
- ii) These are much broader than the normal peaks and
- iii) These are of relatively low abundance.

**Formation of meta stable ions :** consider that  $M_1^+$  is the parent ion and  $m_1^+$  is the daughter ion.

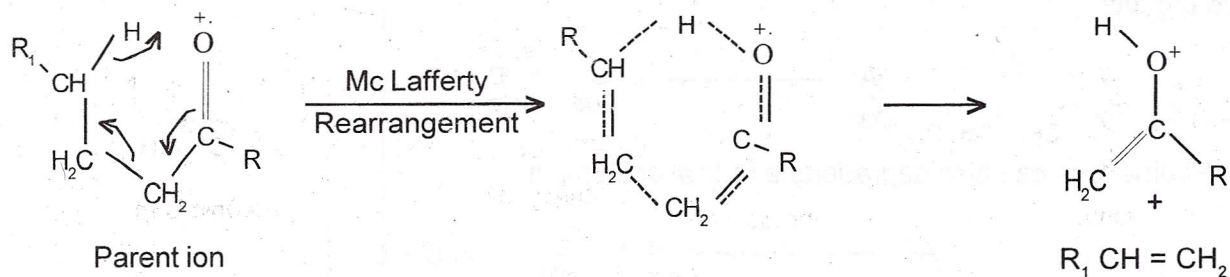
If the reaction  $M_1^+ \rightarrow m_1^+$  takes place in the source, then the daughter ion,  $m_1^+$  may travel the whole analyzer region and is recorded as  $m_1^+$  ion. On the other hand, if the transition  $M_1^+$  to  $m_1^+$  occurs after the source exist and before arrival at the collector, then  $m_1^+$  is called a meta stable ion. The peak for  $m_1^+$  will not appear at the normal position for  $m_1^+$  on the mass scale. Instead the signal appears at  $m_1^2/M_1$ . Hence we conclude that the position of meta stable peak ( $m^*$ ) due to the reaction  $M_1^+ \rightarrow m_1^+$  is such that

$$m^* = m_1^2 / M_1$$

It is important to remember that for a reaction  $M_1^+ \rightarrow m_1^+$ ,  $m^*$  (meta stable peak) has a distance below  $m$ , on the mass scale. The distance is approximately similar to the distance that  $m$  lies below  $M_1$ .

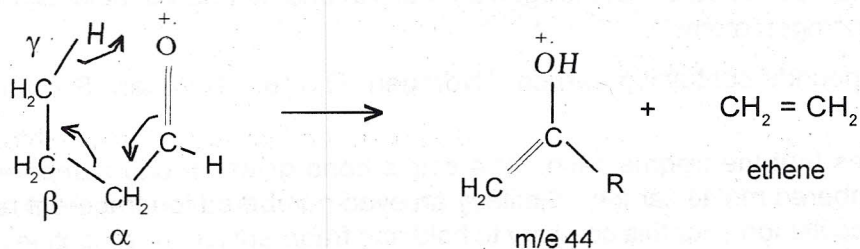
### 2.2.7. Mc Lafferty Rearrangement :

It involves the migration of  $\gamma$ -hydrogen atom followed by the cleavage of a  $\beta$  - bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds through a sterically hindered six membered transition state ex : Ketone.





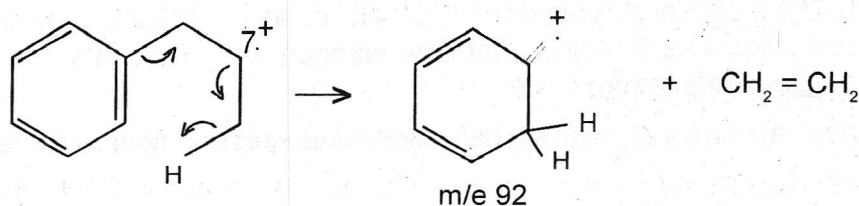
Ex : Butanal



Molecular ion

Thus the molecular formula of the unknown compound can be determined from the various fragment ions and also the parent ion of mass spectrum.

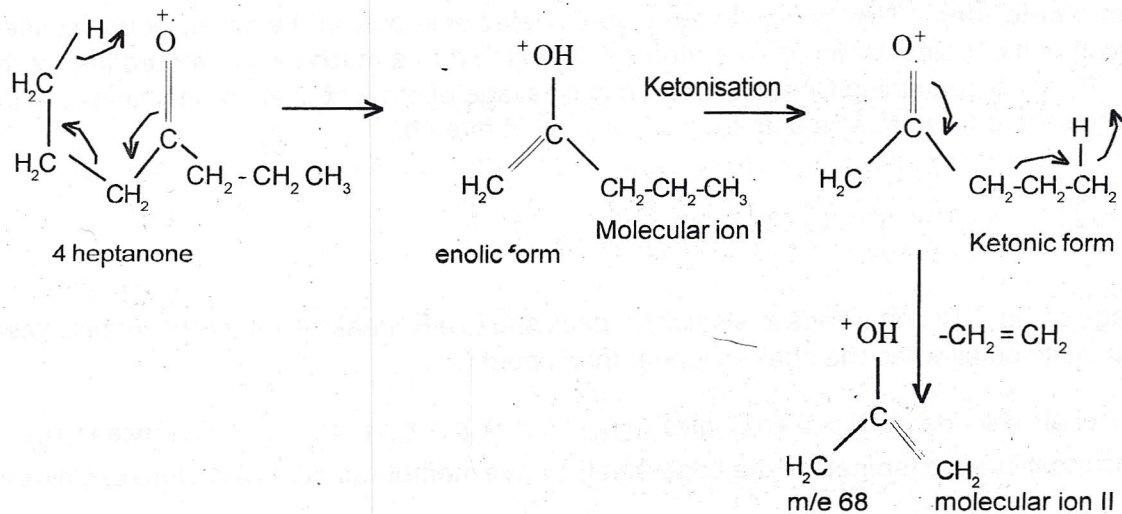
n-Propyl benzene shows a Mc Lafferty rearrangement ion peak in large abundance at m/e 92.



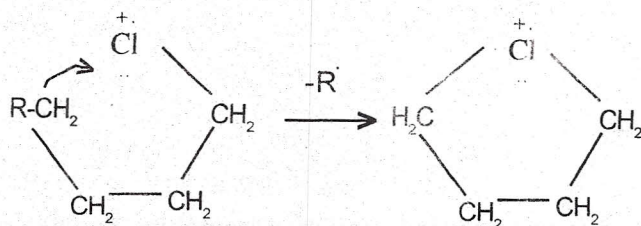
A double Mc Lafferty rearrangement is also reported in certain ketones. The second hydrogen atom originates exclusively from the  $\gamma$ -position. The mechanism involves.

- Ketonisation of the intermediate enol ion by the hydrogen transfer
- Hydrogen transfer to enolic oxygen.

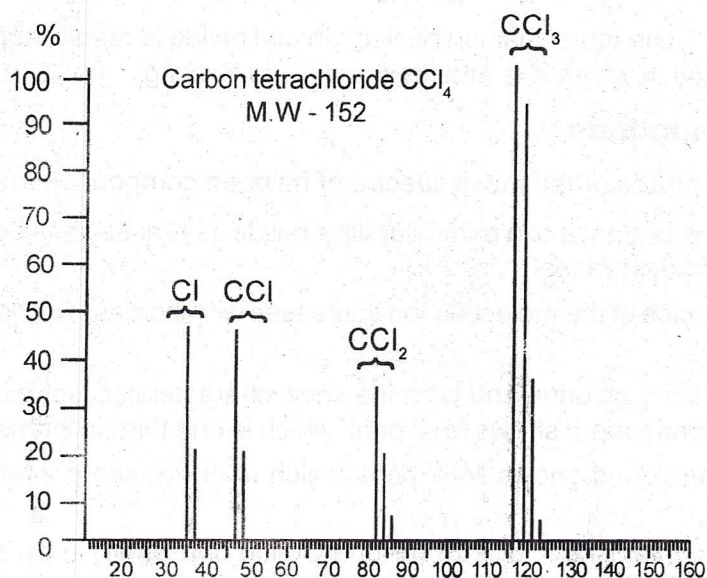
Ex : 4 - Heptanone







Loss of HCl Occurs, possibly by 1,3 elimination to give a peak (Weak or moderate) at M-36



**Aliphatic Bromides** : The remarks under aliphatic chlorides apply to corresponding Bromides.

**Aliphatic Iodides** : They give the strongest molecular ion peak of aliphatic halides. Since  $\text{I}_2$  is mono isotopic, there is no distinctive isotope peak.

Iodides cleave much as do chlorides & bromides but  $\text{C}_4\text{H}_8\text{I}^+$  ion is not as evident as the corresponding chlorides and bromide ions.

**Aliphatic Fluorides** : They give the weakest molecular ion peaks of the aliphatic halides. Fluorine is monoisotopic and its detection in polyfluoro compounds depends on suspicious small isotopic peaks relative to molecular ion, on the intervals between peaks and on characteristic peaks.

Of these the most characteristic is  $m/e$  69 due to ion  $\text{CF}_3^+$  which is the base peak in all perfluoro carbons. Prominent peaks are noted at  $m/e$  119, 169, 219..... these are increments of  $\text{CF}_2$ . The stable ions  $\text{C}_3\text{F}_5^+$  &  $\text{C}_4\text{F}_7^+$  give large peaks at  $m/e$  131 and 181. In mono fluorides cleavage of the  $\alpha\beta$  C-C bond is less important than in other monohalides but cleavage of a C-H bond on the  $\alpha$ -C is more important. This reversal is a consequence of high E.N. of F atom and is rationalized by placing +ve charge on  $\alpha$  carbon. The secondary carbonium ion thus depicted by a loss of a H atom is more stable than the  $\text{I}^\circ$  carbonium ion resulting from loss of an alkyl radical.



relatively more intense. In general, the following group of compounds will be in the order of decreasing ability, give prominent molecular ion peaks.

Aromatic compounds > conjugated alkenes > cyclic compounds > organic sulfides > Short, normal alkanes > mercaptans  
Recognizable molecular ions are usually produced for these compound in order of decreasing ability.

Ketones > amines > esters > ethers > carboxylic acids ~ aldehydes ~ amides ~ halides.

The presence of an M-15 peak (loss of  $\text{CH}_3$ ) or an M-18 peak (loss of  $\text{H}_2\text{O}$  or an M-31 peak (loss of  $\text{OCH}_3$  from methyl esters) and so on, it is taken as confirmation of a molecular ion peak. An M-1 peak is common, and occasionally an M-2 peak (loss of  $\text{H}_2$  by either fragmentation or thermolysis), or even a rare M-3 peak is reasonable.

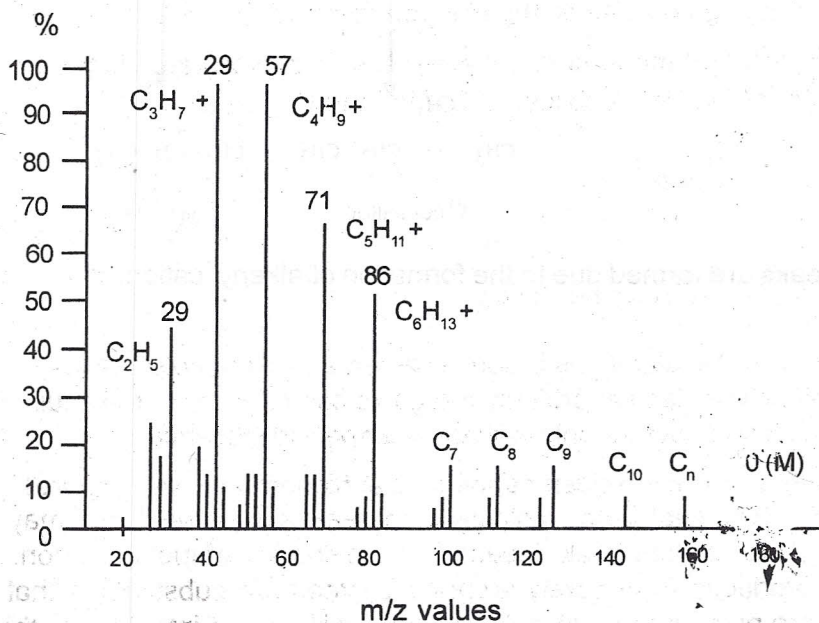
Loss of 16(O), 17(OH), or 18 ( $\text{H}_2\text{O}$ ) are likely only if an oxygen atom is in the molecule.

The intensity of a molecular ion peak is comparatively greatest for straight chain compounds than branched compounds. The intensity of molecular ion peak decreases with increasing molecular weight in a homologous series except fatty acids.

**2.2.10. Alkanes :** The molecular ion will normally be seen in the mass spectra of the lower n-alkanes. But its intensity falls off with increased size and branching of the chain.

Eg : Dodecane

The fragmentation pattern is characterized by Clusters of peaks, and corresponding peaks of each cluster are 14 ( $\text{CH}_2$ ) mass units apart. The largest peak in each cluster represents a  $\text{C}_n\text{H}_{2n+1}$  fragment and this occurs at  $m/z = 14n+1$ , this is accompanied by  $\text{C}_n\text{H}_{2n}$  and  $\text{C}_n\text{H}_{2n-1}$  fragments. The most abundant peaks are produced by  $\text{C}_3\text{H}_7^+$  and  $\text{C}_4\text{H}_9^+$



**Branched Chain Alkanes** : Some important features of the mass spectra of branched chain alkanes are :

Bond cleavage takes place preferably at the site of branching due to such cleavage, a more stable secondary or tertiary carbonium ion results.

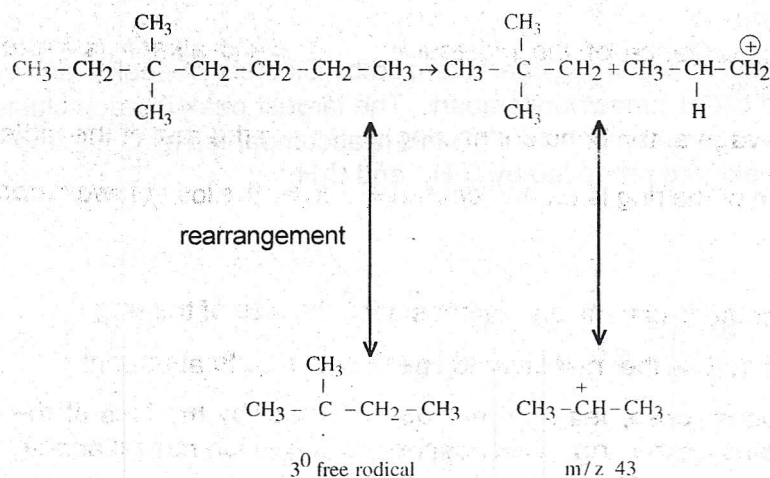
Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by delocalisation of lone electron

Molecular ion is not formed

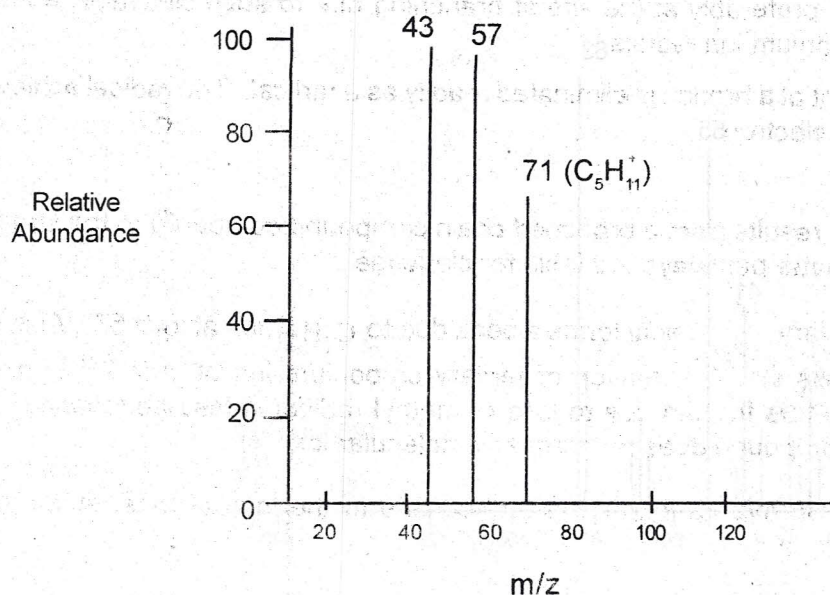
Great number of fragments results from a branched chain compound compared to the straight chain compound. It is due to greater pathways available for cleavage :

As expected, the loss of tertiary radical forms a peak due to  $C_4H_9^+$  ion at 'm/z 57'. Also the loss of n-butyl free radical results in formation of tertiary carbonium ion at 'm/z 71' in much abundance. The peak at 'm/z 71' is formed due to loss of methyl radical in less abundance. As expected, the branched chain compound does not form any molecular ion.

The much abundant peak at 'm/z 43' ( $C_3H_7^+$ ) is formed due to the loss of most stable free radical.



Also small peaks are formed due to the formation of alkenyl cation.



### Cyclo Alkanes :

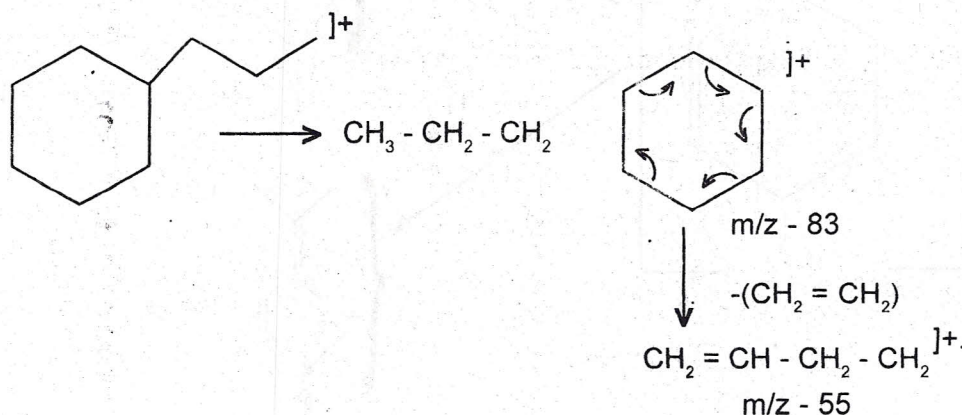
The relative abundance of the molecular ion of cyclo alkane is more as compared to the corresponding alkane.

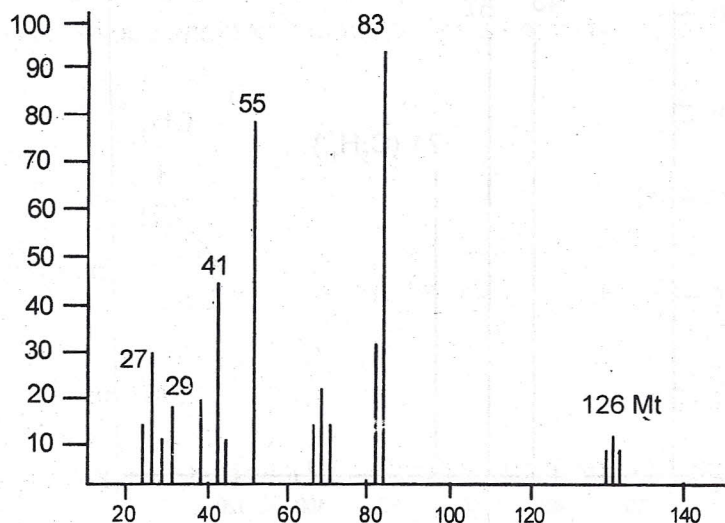
It favours cleavage at the bond connecting the ring to the rest of the molecule.

Fragmentation of the ring is usually characterized by the loss of two carbon atoms as  $C_2H_4$  (28) and  $C_2H_5^+$  (29)

The stability of the fragment ion depends upon the size of the ring.

- The peak m/e 128, is the molecular ion peak and is quite abundant.
- The largest peak (base peak) at 'm/z 83' is formed by the loss of the side chain. The lone electron remains on the ring. This positively charged ion radical appears at m/z 83
- The ion radical shows Retro - Diel's - Alder reaction and fragment ion is formed at 'm/z 55'. The abundance of this ion is very large.





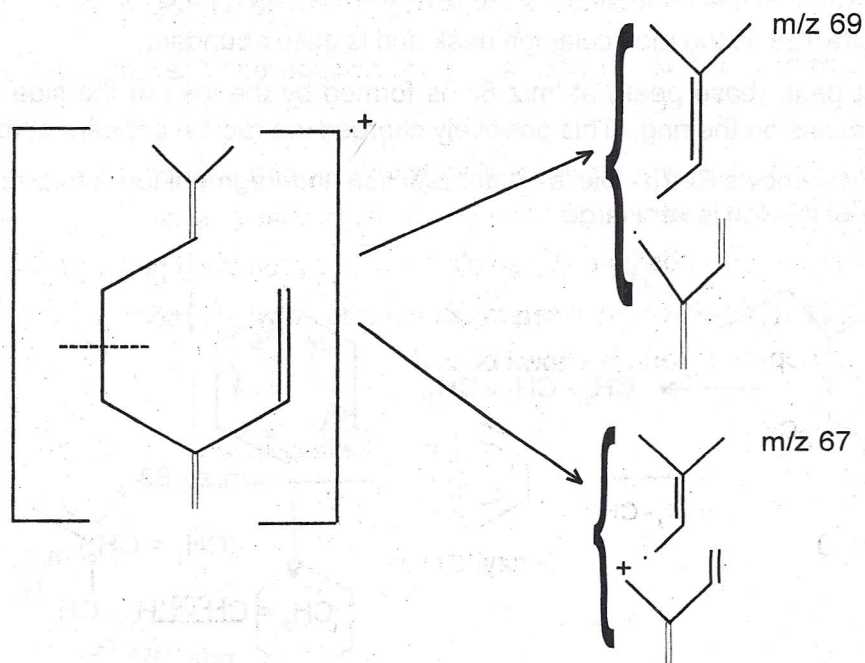
### 2.2.11. Alkenes :

a) The molecular ion peak in the spectra of unsaturated compound is more intense than the corresponding saturated analogues. The reason is the better resonance stabilization of the charge on the cation formed by the removal of one of  $\pi$  - electrons. Mono olefins contain  $C_nH_{2n-1}^+$  ions in their mass spectra.

The relative abundance of the molecular ion peak decreases with increasing molecular mass.

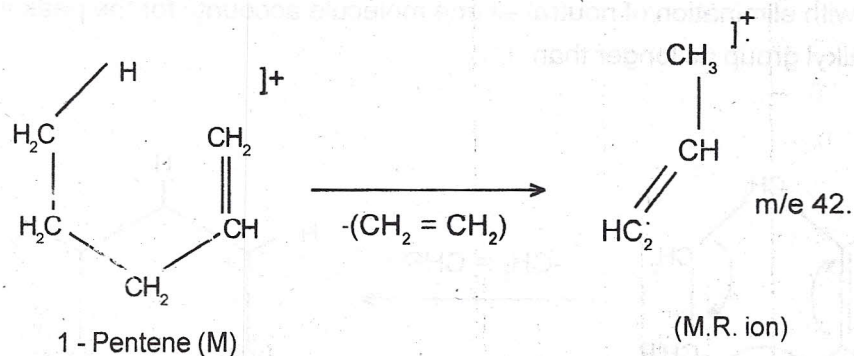
A cyclic olefin also shows group of peaks which are 14 mass units apart.

The general mode of fragmentation induced by a double bond is the allylic cleavage.

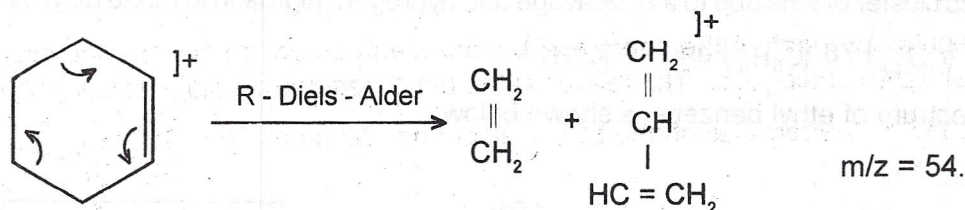




The  $C_nH_{2n}$  ions formed by Mc Lafferty rearrangement are more intense. For example, Mc Lafferty rearrangement ion is formed at  $m/e$  42 from 1-pentene due to loss of ethylene molecule.

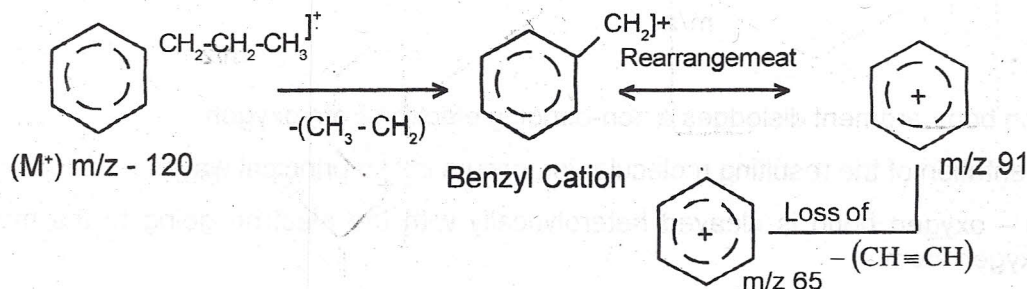


Cyclic olefins usually show a distinct molecular ion peak. They undergo Retro - Diels - Alder reaction.



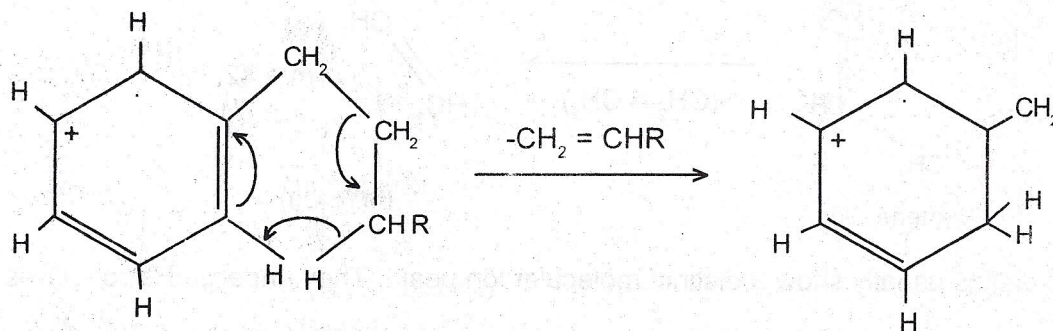
### 2.2.12. Alkyl Aromatic Compounds :

1. The molecular ion peak in aromatic compounds is fairly abundant as compared to the corresponding alkanes and alkenes containing the same number of carbon atoms.
2. In aromatic compounds  $M^+ + 1$  and  $M^+ + 2$  are also noticed. The reason is fairly large abundance of the molecular ion peak.
3. In case of polynuclear hydrocarbons, doubly or triply charged ions ( $M^{2+}$ ,  $M^{3+}$  ions) are possibly formed. Doubly charged molecular ions ( $m/z$ ) appear at integral ' $m/z$ ' values.
4. If the aromatic ring is substituted by an alkyl group, a prominent peak is formed at  $m/e$  91. Here benzyl ( $C_6H_5^+ CH_2$ ) cation formed rearrangements to tropylium cation ( $C_7H_7^+$ ). The fragmentation pattern of *n*-propyl benzene is shown below.



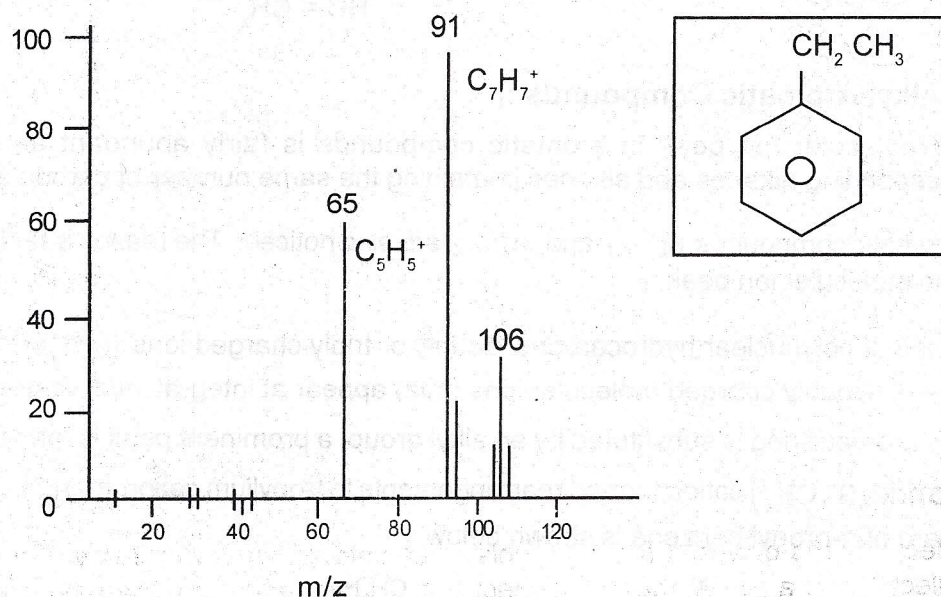
The benzyl cation formed rearranges to more stable tropylium cation which appears at 'm/e 91'. Tropylium cation in turn loses a molecule of acetylene to form  $C_5H_5^+$  at m/e 65.

5. Hydrogen migration with elimination of neutral alkene molecule accounts for the peak at m/z 92 observed when the alkyl group is longer than 'C<sub>2</sub>'.



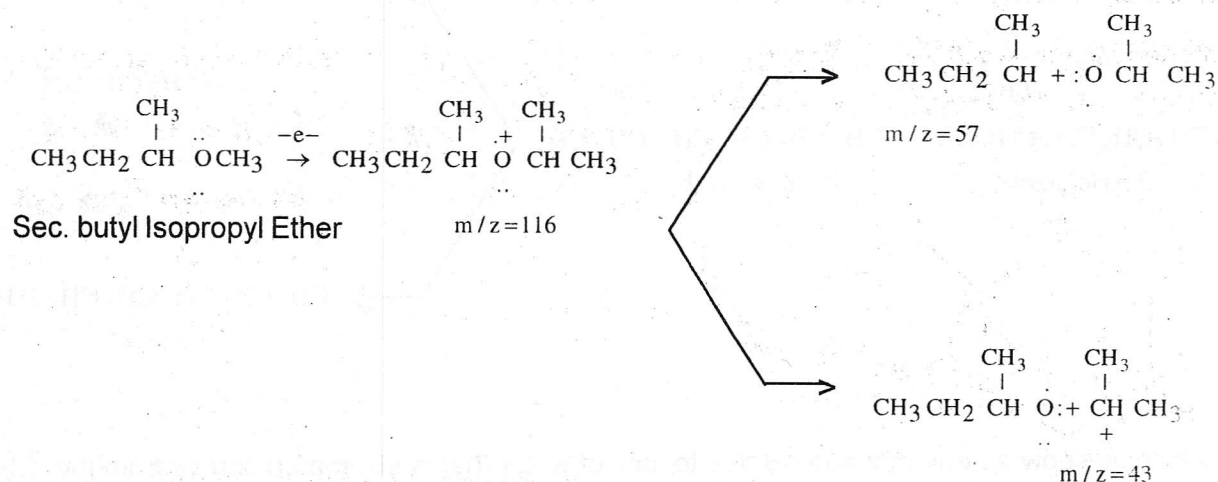
A characteristic cluster of ions due to a  $\alpha$  cleavage and hydrogen migration in mono alkyl benzenes appears at m/z 77 ( $C_6H_6^+$ ), 78 ( $C_6H_6^+$ ) and 79 ( $C_6H_7^+$ ).

The mass spectrum of ethyl benzene is shown below



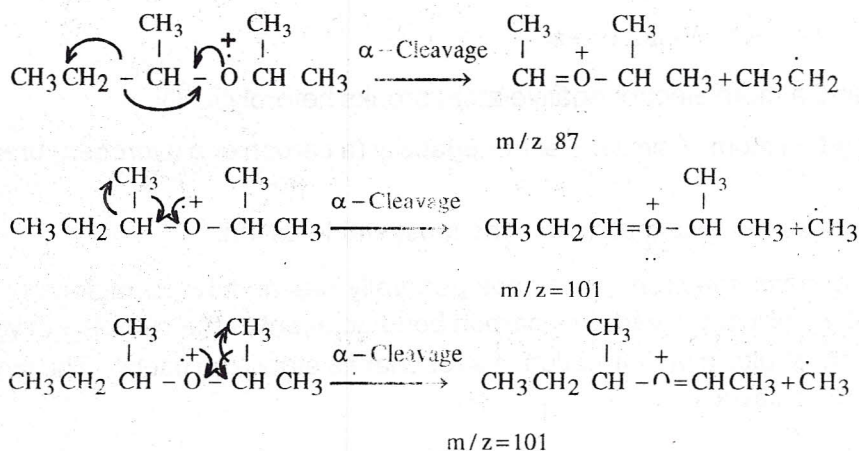
### 2.2.13. Ethers :

1. Electron bombardment dislodges a non-bonding electron from oxygen.
2. Fragmentation of the resulting molecular ion occurs in two principal ways.
  - a) A carbon - oxygen bond is cleaved heterolytically with the electron going to the more electronegative oxygen atom.



$[\text{C}_3\text{H}_7^+]$  ( $m/z = 43$ ) is the molecular ion peak

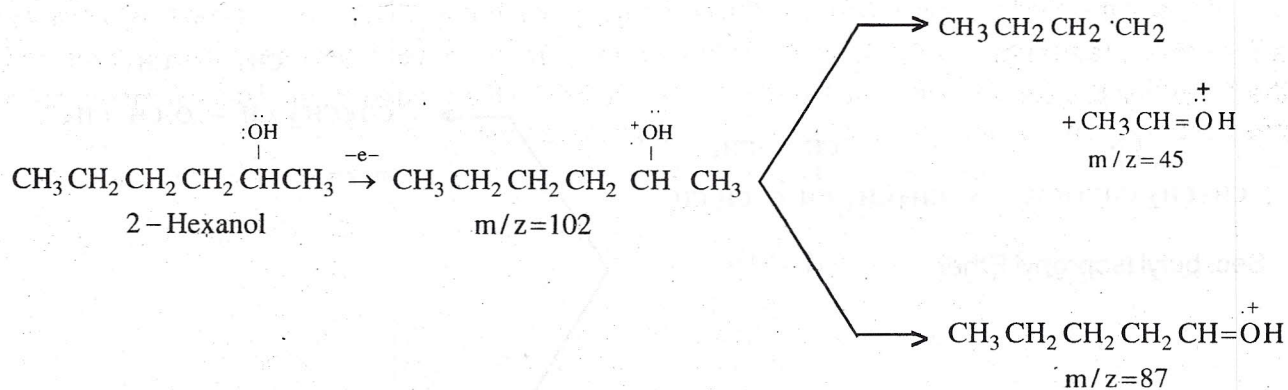
b) A carbon - carbon bond is cleaved homolytically at the  $\alpha$ -position because it leads to a resonance - stabilized cation. The largest  $\alpha$  - substituent is the one most readily cleaved.



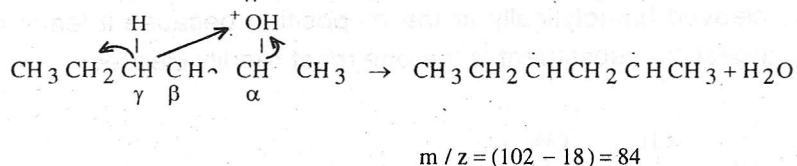
### 2.2.14. Alcohols :

The molecular ions obtained from alcohols fragments so readily that few of them survive to reach the collector. As a result, the mass spectra of primary and secondary alcohols show weak molecular ion peaks, and the molecular ions from  $3^\circ$  alcohols are not detectable.

Alcohols, like alkyl halides and ethers undergo  $\alpha$  - cleavage, with the largest  $\alpha$ -substituent being the one most readily cleaved. Consequently, the mass spectrum of 2-hexanol shows a base peak at  $m/z = 45$  ( $\alpha$ -cleavage of a butyl radical) and a smaller peak at  $m/z = 87$  ( $\alpha$ -cleavage of a methyl radical)

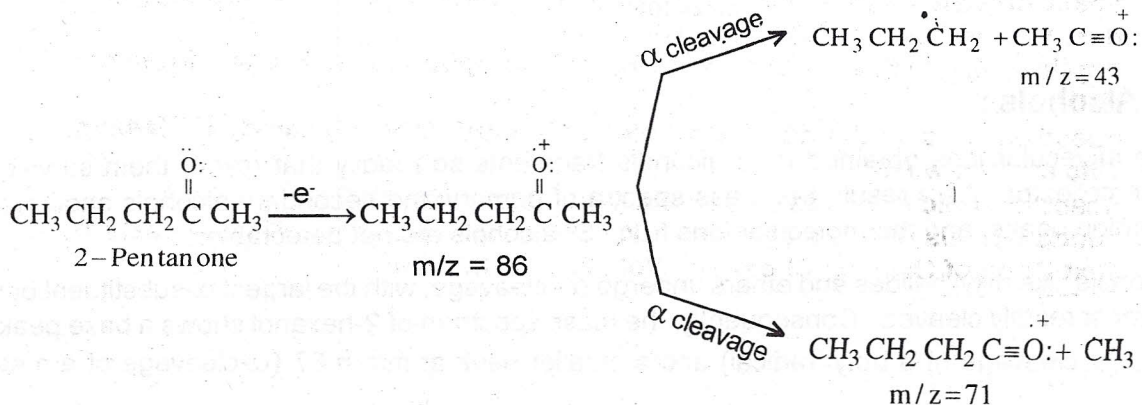


Alcohols show a peak  $m/z = m - 18$  due to loss of water that is eliminated comes from the 'OH' group of alcohol and  $\gamma$  - hydrogen.

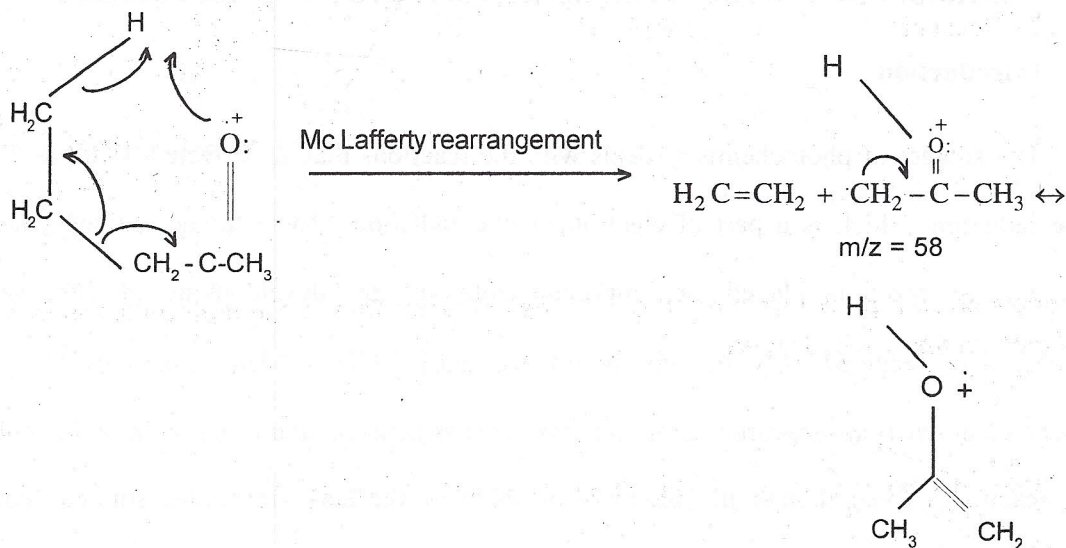


1. A bond between carbon and a more electronegative atom breaks heterolytically.
2. A bond between carbon and an atom of similar electronegativity (a carbon or a hydrogen) breaks homolytically.
3. The bond most likely to break are those that lead to the most stable cation.

**2.4.15. Ketones :** The mass spectrum of ketones generally has an intense molecular ion peak. Ketones fragment homolytically at the carbon - carbon bond adjacent to the carbon - oxygen double bond ( $\alpha$ -cleavage) which results in the formation of a resonance stabilized cation. The larger alkyl group is the one most easily cleaved.



If one of the alkyl groups attached to the carbonyl carbon has a  $\gamma$ -hydrogen, a cleavage known as a 'Mc Lafferty rearrangement' may occur. In this rearrangement the bond between the  $\alpha$ -carbon and the  $\beta$ -carbon breaks homolytically and a hydrogen atom from the oxygen atom. Again, fragmentation has occurred in a way that produces a resonance stabilized cation.



## 2.2.16. Suggested Readings

1. Some Modern methods of Organic Synthesis, W. Carruthers, Cambridge University Press.
2. Advanced Organic Chemistry, Reactions Mechanisms and Structure, J. March. John Wiley
3. Advanced Organic Chemistry Part B, F.A. Carey and R.J. Sundberg, Plenum Press 1.
4. Spectrometric Identification of Organic Compounds, R. M. Silverstein, G.C. Bassler and T. C. Morrill, John Wiley.
5. Applications of Spectroscopy of Organic Compounds, J. R. Dyer, Prentice Hall.
6. Spectroscopic methods in Organic Chemistry, D.H. Williams, I. Fleming, Tata Mc. Graw Hill
7. Spectroscopic methods in Organic Chemistry – Kemp
8. Fundamentals of Photochemistry, K.K. Rohtagi – Mukherji, Wiley – Eastern
9. Text Book of Organic Chemistry Vol I & II – I. L. Finar.